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An apparatus to measure polymer swelling under load

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Abstract

A new apparatus was developed and used to investigate the swelling behavior of crosslinked hydrophilic polymers under an applied load as a function of time and absorbed weight. The swelling capacity and creep compliance of the polyacrylates under load was found to be a function of their degree of crosslinking. The swelling behavior was analyzed as a function of time using the Nutting equation which allowed for a measure of the relative viscous or elastic contributions of the polymer to the creep behavior.

Keywords: Swelling; Swelling force; Poly(acrylic acid); Relaxation; Swelling under load

1. Introduction

Swelling processes are important in a variety of applications including coatings, microlithography, pharmaceutical and biomedical devices (Kuhn, 1967; Peters and Candau, 1988). In many such applications, notably in development of superabsorbent material gels, the polymer swells relatively fast so that measurement of the volume change as a function of time is rather difficult.

Several devices have been developed to measure the swelling behavior. For example, Zasimov et al. (1978) used a simple graduated flask with perforated glass to determine the swelling behavior. Solvent activity and swelling pressure have also been determined (Borchard et al., 1978; Nagy and Horkay, 1980) as a function of time. Dubrovskii et al. (1990, 1994) developed an apparatus using a chamber with a pressure-measuring diaphragm to determine the swelling pressure as a function of time. Alhaique et al. (1993) used a simple glass device to measure weight changes of pharmaceutical formulations. We have also developed (Catellani et al., 1989; Khare et al., 1992) techniques that can measure the swelling force as a function of time.

Most of these techniques present the problem that they cannot measure the swelling of polymer microparticles or disks under load. Such a method would be important in simulating swelling processes where a preapplied load is used, as for example in testing of superabsorbent polymers (Brannon-Peppas and Harland, 1990).

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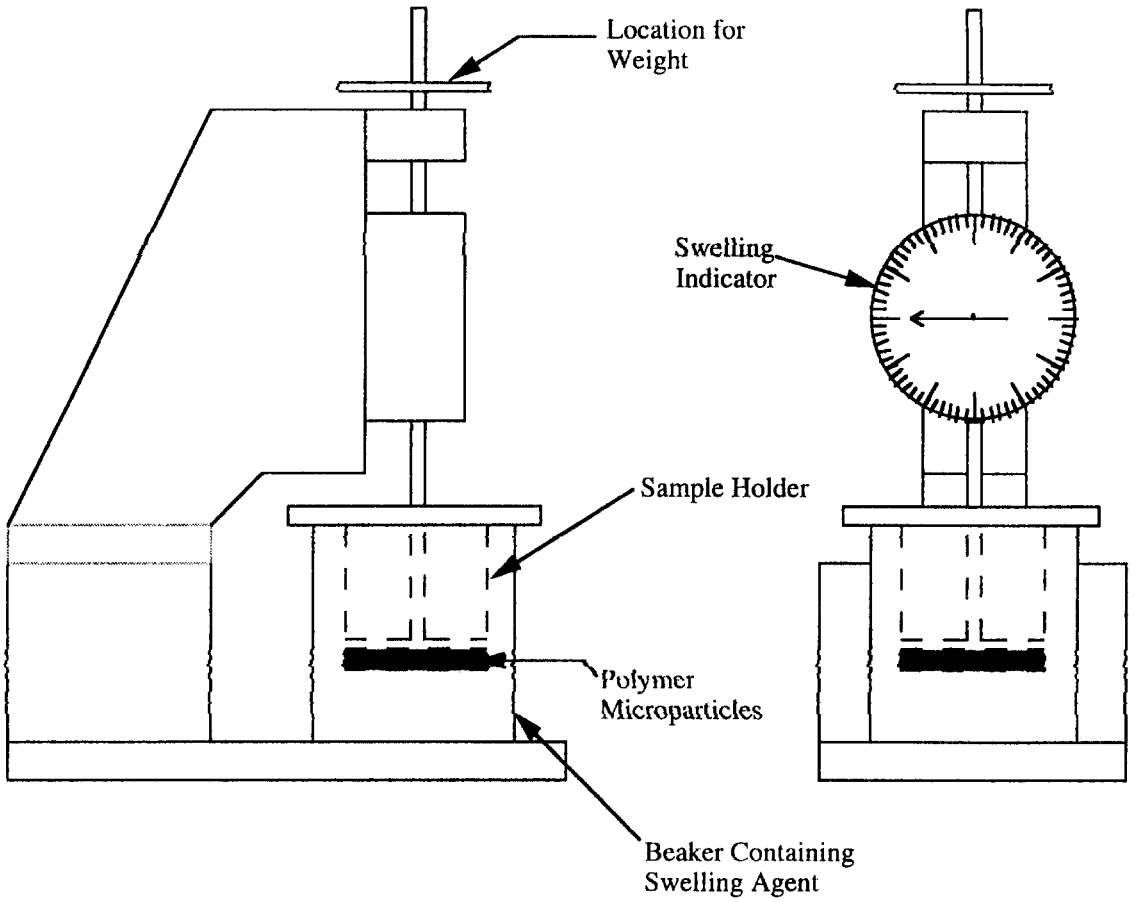

Fig. 1. Device for measuring swelling behavior of polyacrylate microparticles under load.

2. Experimental

Crosslinked polyacrylates were synthesized by solution polymerization. The acrylic acid monomer (Aldrich Chemical Co. Inc., Milwaukee, WI) was vacuum distilled for purification and partially neutralized using a 0.2 M NaOH solution. The crosslinking agent was trimethylolpropane triacrylate (TMPTA, Sigma Chemical Co. Inc., St. Louis, MO) and a redox initiator of sodium metabisulfite and ammonium persulfate was used. The reaction mixture was diluted to a 35% aqueous solution and stirred well. Polymerization occurred in polypropylene vials at 37°C for 24 h. The polyacrylates were then dried in a vacuum oven at 40°C. When dry, the polyacrylates were ground into microparticles of 30–50 mesh.

A new device (shown in Fig. 1) was developed to measure swelling under load. In these experiments, 0.5 g of polyacrylate microparticles were placed on the wire mesh of 100 mesh size in the bottom of the sample holder. The particles were then spread out as uniformly as possible on the wire mesh, and a Teflon cover was placed on top of the sample. The sample holder was then suspended in a beaker as shown, and placed under the measuring device such that the plunger of the device rested on the sample cover and the measuring dial read zero. A weight of 76 g was then added on the measuring device as shown in the diagram. The Teflon cover weighed 27 g. The beaker was then filled with 300 ml of 0.9% saline solution. Saline was added through the lip of the

beaker using a syringe, and the wire mesh portion of the sample was, as a result, immersed in the saline solution. The swelling process was started when the saline came into contact with the wire mesh. As the polymer microparticles swelled against the load, the height on the measuring dial was taken at various time increments until there was less than a 25.4 μm height change over a 5 min period.

3. Results and discussion

The swelling behavior of microparticles of all of the polyacrylate samples was investigated in saline under a load of 103 g. This was done by measuring the height change of the sample as swelling occurred under the load using the device described earlier. The thickness (height) change was then translated into a volume change using the following relation

$$V_s = h_s\left[\frac{\pi D^2}{4}\right] \tag{1}$$

where V_s is the volume of the swollen gel, h_s is the height of the swollen gel as measured by the swelling under load device, and D is the approximate diameter of the sample. The diameter was measured as an average value of 4.45 cm. The volume of the dry sample, V_d, was determined from equation (1) using the initial thickness or height (kept constant at 0.0297 cm) of the sample in place of h_s.

From these data, the volume degree of swelling, Q, was determined by equation (2)

$$Q = \frac{V_s}{V_d} \tag{2}$$

The swelling capacity under load, q, may also be determined from these data using the following expression

$$q = (Q-1)\frac{\rho_s}{\rho_p} \tag{3}$$

Here, ρ_s and ρ_p are the densities of the saline solution and the polymer, respectively. The density of the polymer was measured experimentally and found to be 1.277 g/cm^3. The density of the saline was assumed to be 1 g/cm^3.

Fig. 2 shows typical data of the swelling under load, Q, as a function of time for 40% neutralized polyacrylate samples tested. As seen, the microparticles swelled rapidly at short times, but the swelling rate eventually levelled off. It is also interesting to note the differences between samples of different nominal crosslinking ratios. Samples of higher crosslinking ratios could not expand as far as the more loosely crosslinked samples because the networks were held together more tightly by the chemical crosslinks. For the same reason, the swelling ratio of the samples of higher crosslinking ratio levels off faster than that of the samples with lower crosslinking ratios. The swelling results of samples containing 60% neutralization were similar in nature.

Swelling under load data may also be analyzed to determine the crosslinking density of the polyacrylate samples. For this purpose, the effective network chain concentration, ν_e/V, defined as the moles of crosslinked chains per unit volume of swollen gel, was determined using the relation

$$\frac{\nu_e}{V} = \frac{\upsilon_{2,s}^{1/3}\sigma_o}{RT(\alpha - \alpha^{-2})} \tag{4}$$

Here, $\upsilon_{2,s}$ is again the volume fraction of polymer in the swollen gel, σ_o is the applied stress (= 498.52 N/m^2), R is the gas constant, T is the absolute temperature, and α is the elongation, or

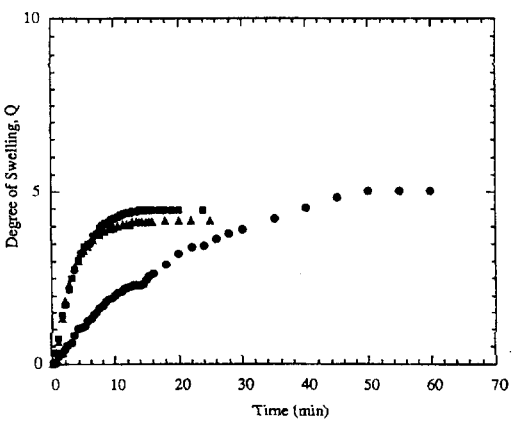

Fig. 2. Degree of swelling (vol. swollen PAA/vol. dry PAA) of 40% neutralized polyacrylate microparticles in saline at 25°C under a load of 103 g. Nominal crosslinking ratios were X = 0.001 (●), X = 0.005 (■), and X = 0.01 (▲).

Table 1
Experimental values of crosslinking density and molecular weight between crosslinks determined from swelling under load

Degree of AA neutralization during polymerization	Crosslinking ratio X (mol TMPTA/mol AA)	Crosslinking density v_e/V	Molecular weight between crosslinks M_c
60	0.001	0.0274	37 473
60	0.005	0.0325	37 468
60	0.01	0.0400	37 460
40	0.001	0.0281	37 472
40	0.005	0.0330	37 467
40	0.01	0.0368	37 464

the ratio of the equilibrium height to the initial height.

From the value of crosslinking density, v_e, the molecular weight between crosslinks was determined using the expression

$$\frac{1}{\bar{M}_c} = \bar{\upsilon}\frac{v_e}{V} + \frac{2}{\bar{M}_n} \tag{5}$$

where $\bar{M}_n$ is the number average molecular weight of the uncrosslinked polymer, and $\bar{\upsilon}$ is the specific volume of the polymer. Table 1 summarizes the results of these calculations for the polyacrylate samples. The correlation between nominal crosslinking ratio and molecular weight between crosslinks is not as significant as might have been expected. This is probably due to the fact that this analysis is used in analysis of polymers which exhibit lower extension ratios whereas the systems studied here swelled to very large extension ratios. However, the value of $\bar{M}_c$ determined from the swelling under load calculations decreased slightly as the crosslinking ratio increased as expected.

The data obtained from the swelling under load experiments were also analyzed using a mechanical theory applied to compressive creep analysis. First, the stress applied to the sample was constant and determined by the relation

$$\sigma_o = \frac{W}{\pi D^2/4} \tag{6}$$

where W is the applied load (= 103 g), and D is again the diameter of the sample tested. The dynamic strain of the sample, $\gamma(t)$ was evaluated by

$$\gamma(t) = \frac{\Delta h}{h_0} = \frac{h(t) - h_0}{h_0} \tag{7}$$

where $h(t)$ is the height of the sample at time t, and h_0 is again the initial height of the sample. Using these results the creep compliance, $J(t)$ was calculated.

$$J(t) = \frac{\gamma(t)}{\sigma_o} \tag{8}$$

Fig. 3 shows the results of this analysis for the 40% neutralized polyacrylate samples. Clearly, the rate of compressive creep, as seen by the behavior of the compliance as a function of time is high at short times and gradually decreased to near zero. This was logical because of the fast initial swelling (deformation) rate of these polyacrylates. The time-dependent compliance increases rapidly at

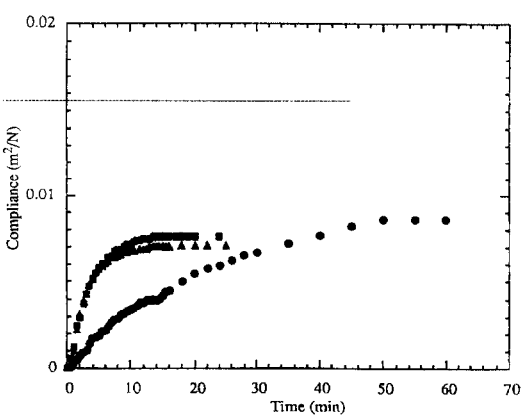

Fig. 3. Creep compliance of 40% neutralized polyacrylate microparticles in saline at 25°C under a load of 103 g. Nominal crosslinking ratios were X = 0.001 (●), X = 0.005 (■), and X = 0.01 (▲).

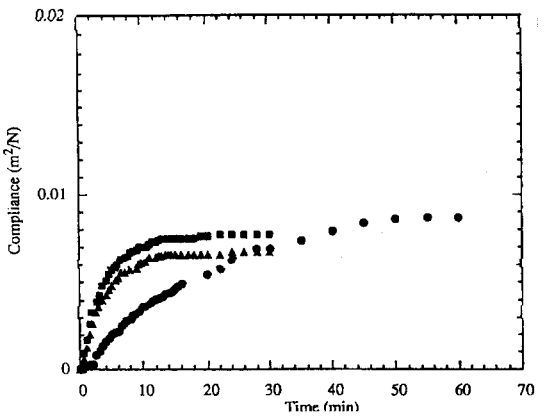

Fig. 4. Creep compliance of 60% neutralized polyacrylate microparticles in saline at 25°C under a load of 103 g. Nominal crosslinking ratios were X = 0.001 (●), X = 0.005 (■), and X = 0.01 (▲).

first as the microparticles swell rapidly pushing the load upward and then levels off as the samples reach the point at which they are unable to expand any further when the compliance reaches an equilibrium value. The results of the compliance analysis of the 60% neutralized polyacrylates are shown in Fig. 4.

Another way of analyzing this creep data is to apply the Nutting theory to the results in order to evaluate the elasticity of the polyacrylate networks. The Nutting theory applies to approximately the first 60% of the compressive creep data, that is in the region where the creep rate is linear. The Nutting equation is expressed as follows:

$$J(t) = \psi t^n \tag{9}$$

where ψ and n are constants. The exponent n can vary between zero and one and is a measure of the relative viscous and elastic contributions of the polymer to the creep behavior. If n equals zero, the material is considered perfectly elastic while if n is one, the polymer acts as a viscous liquid.

Table 2 shows the results of this analysis for the polyacrylates. As seen in the table, all of the polyacrylates exhibit very elastic properties during the swelling under load experiments. This is logical behavior for polymeric networks that swell to a high degree.

4. Conclusions

A novel swelling apparatus was developed and used to determine the swelling process under an applied load (stress). The swelling capacity and creep compliance of crosslinked polyacrylates under load was found to be a function of their degree of crosslinking. Using Nutting theory analysis, the polyacrylates were found to exhibit very elastic properties during swelling under load.

Acknowledgements

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Table 2
Nutting exponent, n, of polyacrylate microparticles during swelling under load

Degree of AA neutralization during polymerization	Crosslinking ratio X (mol TMPTA/mol AA)	Nutting exponent n
60	0.001	0.0003
60	0.005	0.0014
60	0.010	0.0012
40	0.001	0.0002
40	0.005	0.0015
40	0.010	0.0019

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